



# Simulation and experimental study on the desulfurization for smelter off-gas using a recycling Ca-based desulfurizer



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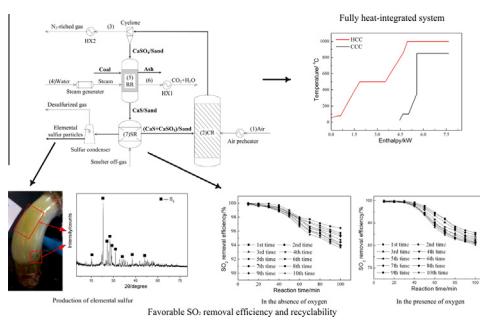
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## HIGHLIGHTS

- The system could keep the autothermal operation with a high SO<sub>2</sub> removal efficiency.
- The SO<sub>2</sub> removal efficiency is higher than 99.5% at a temperature from 500 °C to 580 °C.
- The elemental sulfur powders are obtained after the desulfurization.
- Both the SO<sub>2</sub> removal efficiency with and without O<sub>2</sub> are satisfactory in ten cycles.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 12 September 2015

Received in revised form 4 December 2015

Accepted 21 December 2015

Available online 24 December 2015

### Keywords:

Smelter off-gas  
Desulfurizer  
SO<sub>2</sub> removal efficiency  
Recyclability

## ABSTRACT

In this paper, a novel desulfurization process was proposed to recover elemental sulfur from smelter off-gas with high-content sulfur dioxide (SO<sub>2</sub>) using calcium sulfate (CaS) as a new recycling Ca-based desulfurizer. Based on the simulation results, an optimum temperature range between 450 °C and 550 °C was determined. In that range a high SO<sub>2</sub> removal efficiency was obtained for the smelter off-gas, indicating that all the SO<sub>2</sub> gas was converted to elemental sulfur. To achieve autothermal operation of the whole process, a suitable range was identified for the circulating ratio of quartz sands used as the heat carriers. The practicality of Ca-based desulfurizer was tested through the multi-cycle desulfurization/regeneration tests. High temperature was favorable for the improvement of the SO<sub>2</sub> removal efficiency, which was higher than 98.5% in the initial desulfurization period at the temperature above 500 °C. However, increasing the space velocity would reduce the SO<sub>2</sub> removal efficiency, especially at the late period of desulfurization. The desulfurizer showed a good recyclability in the multi-cycle tests for both the off-gas with and without oxygen. Both the SEM images and energy dispersive X-ray analyses proved that the desulfurizer particles showed good multicycle stability and recyclability. Both the Raman spectroscopy and the EDS spectrum of the collected sulfur particles indicated that the sulfur particles were composed of the orthorhombic  $\alpha$ -S<sub>8</sub> species and the amorphous  $\mu$ -S species. The desulfurizer particles slightly agglomerated over the repeated cycles from both the particle surface area analysis and the particle size distribution analysis.

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## 1. Introduction

Modern pyrometallurgical smelter processes for sulfide ores based on the use of oxygen-enriched air produced relatively small

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smelter off-gas flows with high levels of sulfur dioxide ( $\text{SO}_2$ ). The  $\text{SO}_2$  concentration was even higher than 20% by volume [1,2].  $\text{SO}_2$  combined with moisture in the atmosphere and thus formed dilute solutions of sulfuric acid or “acid rain”. Acid rain caused direct damages to forests, crops and lakes and also had a synergic negative action when combined with gaseous pollutants and particulates in the atmosphere [3,4]. As stringent environmental regulations regarding  $\text{SO}_2$  emissions have been enacted in many countries,  $\text{SO}_2$  is now being removed from the flue gases produced by the combustion of fossil fuels by flue gas desulfurization (FGD) technology.

Based on the desulfurizer being used, the conventional FGD technology involved calcium-based technology (limestone/lime), ammonia-based technology, magnesium-based technology, sodium-based technology, alkali alumina-based technology, copper oxide/zinc oxide-based technology, active carbon-based technology, ammonium dihydrogen phosphate-based technology and so on. Among them, the calcium-based technology has been predominantly selected over other FGD technologies for two principal reasons: its high desulfurization efficiency and vastly available desulfurizers. However, it was mostly used to remove  $\text{SO}_2$  in the flue gas from coal-fired boilers with a concentration of  $\text{SO}_2$  lower than 5000 ppm [5]. Actually, it was more reasonable and economical to recover the high concentration of  $\text{SO}_2$  from the smelter off-gas rather than remove the  $\text{SO}_2$ . Additionally, all the conventional FGD technologies have not yet been proven to be effective for the smelter off-gas with high concentration of  $\text{SO}_2$ .

To abate  $\text{SO}_2$  emissions and recover sulfur, most of the smelters were usually coupled with the sulfuric acid plants to convert  $\text{SO}_2$  to sulfuric acid rather than choose FGD methods to remove  $\text{SO}_2$ . However, the smelter off-gas must be primarily diluted down to a suitable  $\text{SO}_2$  concentration of 12–14% by adding large amounts of air [6]. Too high  $\text{SO}_2$  concentration would cause a reaction temperature exceeding the allowable limit for the catalyst in the catalytic oxidation step. As a consequence, many large equipments were placed in those acid plants, characterized by high capital cost, high energy consumption and limited flexibility. Additionally, the sulfuric acid capacity was serious surplus in China. For instance, in 2012, the sulfuric acid productive capacity hit 106 million MT per year with only 80% of the capacity utilized [7], making many smelters struggle to dispose of the sulfuric acid. With such insecurity in the acid market it was important for the smelters to look for an alternative method to fix  $\text{SO}_2$ .

Actually, the elemental sulfur was the desirable end product for the  $\text{SO}_2$  producers located far away from their customers, since it was easier to handle, store and transport than sulfuric acid. Up to now, the selective catalytic reduction of  $\text{SO}_2$  to elemental sulfur has been frequently studied for the flue gas from the power plants [8–15]. In the processes, carbon monoxide ( $\text{CO}$ ), hydrogen ( $\text{H}_2$ ) or methane ( $\text{CH}_4$ ) is used as a gaseous reductant in the presence of a catalyst. The most commonly used catalysts involved V–Sb–Ce/TiO<sub>2</sub> [8], Co–Mo–S/γ-Al<sub>2</sub>O<sub>3</sub> [9], V<sub>2</sub>O<sub>5</sub>/CNT [10], combined Na<sub>2</sub>SO<sub>3</sub> assisted electrochemical reduction [11], Ce–Fe/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> wire-mesh honeycomb catalyst [12], Sn–Zr–O catalyst [13], Ce/TiO<sub>2</sub>–20SiO<sub>2</sub>–3.5Al<sub>2</sub>O<sub>3</sub> [14], MnCo<sub>2</sub>O<sub>4</sub> [15] and so on. The multimetallic catalysts were effective in the presence of the flue gas with a low  $\text{SO}_2$  concentration. However, the high  $\text{SO}_2$  concentration in the smelter off-gas would rapidly age the catalyst. Additionally, the gaseous reductant must be controlled excessive to  $\text{SO}_2$  to achieve a favorable  $\text{SO}_2$  conversion, whereas lead to the production of some by-products, such as sulfureted hydrogen ( $\text{H}_2\text{S}$ ) and carbonyl sulfide ( $\text{COS}$ ).

Sohn [16–19] proposed a novel method for converting high concentration of  $\text{SO}_2$  to elemental sulfur using the CaS/CaSO<sub>4</sub> and BaS/BaSO<sub>4</sub> cycle. In the TGA experiments calcium sulfide (CaS) or barium sulfide (BaS) was used as a desulfurizer to convert  $\text{SO}_2$  to

elemental sulfur. The spent desulfurizer, in the form of calcium sulfate (CaSO<sub>4</sub>) or barium sulfate (BaSO<sub>4</sub>), was in turn reduced by hydrogen and regenerated to the sulfides. The method offered some clear advantages over the acid method. Firstly, no expensive catalyst was used in the sulfur recovery process, and so the capital cost would decrease sharply. Secondly, high concentration of  $\text{SO}_2$  was treated with the sulfides safely and conveniently without any large scale equipments. Thus, the flexibility of the system could be greatly improved. Finally, the method is environment-friendly and both the waste water and solid wastes were eliminated. However, few information was available in the published papers on the reactivity of the desulfurizer in the reactors. Additionally, as a respected tool for minimizing energy consumptions and optimizing operating conditions of chemical processes, the heat integration analysis was not performed for a whole desulfurization system in the papers. Thus, the system involving CaSO<sub>4</sub>/CaS cycles was not yet proven technically feasible.

In this paper, we proposed a system comprised of desulfurization of smelter off-gas and regeneration of desulfurizer in conjunction with the steam-coal gasification. An optimum operating regime was defined to keep the whole system autothermally operating without any external heat addition, while achieving satisfactory  $\text{SO}_2$  removal efficiency. A series of multicycle desulfurization/regeneration experiments were also performed in a quartz fixed-bed reactor to investigate the  $\text{SO}_2$  removal efficiency of the desulfurizer.

## 2. Methods and model details

A flowsheet for the whole desulfurization system involving three interconnected reactors was conceived and displayed in Fig. 1. All the possible reactions occurred in the reactors was listed in Table 1. In the SR reactor, the CaS particles reduced the  $\text{SO}_2$  in the smelter off-gas to elemental sulfur. The desulfurization temperature in SR reactor was higher than the boiling point (447.64 °C) of elemental sulfur, so the sulfur would be released in the form of mixed sulfur vapors, such as S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub> and so on [20]. When the exhaust gas from SR reactor was cooled and condensed, the sulfur particles could be obtained in a separate heat exchanger, commonly referred to as a sulfur condenser [21]. The sulfur condenser was commonly used to collect the solid or liquid sulfur in Claus Process of the gas processing factory, the refinery and petroleum production sites. It was feasible and applicable in industry. Therefore, the construction investment of the sulfur collection method was lower than the conventional wet FGD method. To obtain a high  $\text{SO}_2$  removal efficiency, CaS species was excessive to  $\text{SO}_2$  in SR. Then, the partly oxidized desulfurizers entered CR reactor and were further oxidized to CaSO<sub>4</sub> with a quantity of air, which was a highly exothermic reaction. Among the reactors in the system, the reaction temperature in CR was highest. When a large body of non-combustible hot solid particles, including desulfurizer and sand, moved from CR to RR, they could heat the cold coal powders in RR close to the gasification temperature. Therefore, CR was regarded as a heat source to provide the heat required by steam gasification of coal in RR. Similarly, the hot bed materials could also adjust the smelter off-gas close to the bed temperature in the SR reactor even if the temperature of the smelter off-gas varied. When the smelter off-gas flowed up in the form of bubbles through the bed, these hot bed materials would immediately engulf the bubbles. Therefore, the bed could reach a uniform temperature due to the good gas-to-particle heat transfer ability.

In the RR reactor, the spent desulfurizers, in the form of the sulfates, were reduced to the sulfides by the syngas from steam gasification of coal. Both the gasification of coal and the regeneration of desulfurizer could take place in the same reactor, which was

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